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Using Isotope Dilution Mass Spectrometry to Determine Aqueous Trichloroacetic Acid

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16. ABSTRACT

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EPA/600/J-86/134
JOURNAL ARTICLE

Using Isotope Dilution Mass Spectrometry to Determine Aqueous Trichloroacetic Acid

Daniel L. Norwood, Russell F. Christman, J. Donald Johnson, and J. Ronald Hass

The development, verification, and application of a method based on isotope dilution gas chromatography–mass spectrometry to determine aqueous trichloroacetic acid (TCAA) at the micrograms-per-litre level are described. The simultaneous determination of aqueous chloroform is also demonstrated. Trichloroacetic acid is shown to be a significant by-product of the chlorination of raw waters in the laboratory and to constitute a large fraction of the total organic halide (TOX) formed. Analysis of finished-water samples indicated that TCAA, like trihalomethanes, is ubiquitous. Positive correlations exist between the levels of TCAA in laboratory-chlorinated raw waters and in finished waters and measured TOX.

It is well documented that chloroform ($CHCl_3$) is a major product of the reaction between aquatic humic substances and aqueous chlorine. The occurrence of precursor humic substances in natural waters is believed to account for the presence of $CHCl_3$ and other trihalomethanes (THMs) in drinking waters disinfected with chlorine. However, some reports indicate that THMs cannot account for the major part of the total organic halide (TOX) produced from isolated humic material[1] and in chlorinated raw water samples.[2,3] These results suggest that a significant fraction of the TOX is composed of nonvolatile, hydrophilic compounds.

Several studies that have been performed in the authors' laboratory have shown that chlorination of isolated aquatic humic material produces a wide variety of nonvolatile chlorinated compounds,[4-7] including chlorinated aliphatic mono- and dibasic acids and unchlorinated aromatic acids. In all cases, trichloroacetic acid (TCAA) was the dominant structure found. Yield studies[7] confirmed that TCAA was the dominant product and indicated that the sum of TCAA and $CHCl_3$ accounted for about 50 percent of the TOX produced. Uden and co-workers reported similar results for other humic materials[8,9] and demonstrated the relative production of TCAA and $CHCl_3$ to be a function of various reaction parameters.[9]

The realization that TCAA could be present in drinking water at levels similar to those of THMs has stimulated the development of specific methods for determining this compound at the micrograms-per-litre level. Uden and co-workers reported a method based on liquid–liquid extraction of TCAA coupled with capillary gas chromatography and element-specific detection.[10] Several applications of this method, including the analysis of drinking water samples, have been reported.[8,9,11] Results of these studies showed that both di- and trichloroacetic acids were present in two Amherst, Mass., tap water samples at levels similar to those of chloroform.[11]

This article describes the development, verification, and application of a specific method for determining TCAA at the micrograms-per-litre level based on isotope dilution gas chromatography–mass spectrometry (GC–MS). An advantage of the method is that $CHCl_3$ can be determined with the same extraction and cleanup procedure.

Isotope dilution mass spectrometry involves the use of stable isotopically labeled internal standards for specific analytes contained in a matrix. These internal standards can significantly reduce systematic error (bias) from several sources, including sample instability prior to analysis, interference or matrix effects, and the calibration procedure. The technique has long been utilized in the biomedical field,[12] and Colby and Rosencrance[13] recently demonstrated its applicability to priority pollutant analysis.

Experimental methods

Sample collection. Samples of raw water for chlorination in the laboratory were collected in chromic-acid-washed 1-L glass bottles and stored until needed at room temperature in a headspace-free condition. Samples of each raw water source were also collected in acid-washed, 60-mL, septum (PTFE)-capped glass vials for total organic carbon (TOC) analysis.* The sample utilized as a test matrix for the method verification experiments was taken from a 150-gal (568-L) sample of lake water, which was at that time being used as a source of extracted aquatic humic material for other studies. This particular sample was obtained from Black Lake, a highly colored surface water located near Elizabethtown, N.C.

Drinking water samples for TOX screening were also collected in acid-washed, 1-L glass bottles and returned to the laboratory in a headspace-free condition. Grab samples were taken from drinking water taps, with no effort being made to normalize time in the distribution system. In the laboratory, residual chlorine was removed by adding sodium arsenite crystals that had previously been Soxhlet-extracted for 24 h with diethyl ether to remove potential contaminants. Two 60-mL samples were then removed, placed in septum-capped vials, and analyzed for TOX according to US Environmental Protection Agency (USEPA) Interim Method 450.1.[14] Standard-addition experiments with chlorinated Black Lake fulvic acid matrix have shown that 93 percent of TCAA and 75 percent of $CHCl_3$ are recovered as TOX by this method.

Chlorination. Chlorination was performed by adding varying amounts of 5-percent sodium hypochlorite† to the raw water samples. After chlorine was added, each mixture was acidified to near-neutral pH with concentrated hydrochloric acid (HCl). Headspace-free conditions and ambient temperatures were maintained in all cases over a 24-h

*Dohrman DC-80, Dohrman Inc., Santa Clara, Calif.
†Fisher Scientific, Raleigh, N.C.

TABLE 1
Formulas for isotope dilution calculations[16]

Equation	Acceptable Application Window*
(1) $x/y = R_m$	$10R_y < R_m < 0.1\,R_x$
(2)† $x/y = \dfrac{(R_y - R_m)(R_x + 1)}{(R_m - R_x)(R_y + 1)}$	$2R_y < R_m < 0.5\,R_x$

R_x = isotope ratio for compound
R_y = isotope ratio for labeled analogue
R_m = isotope ratio for analytical mixture
x/y = mole ratio

*Acceptable is defined as <±10-percent error, assuming ±5-percent measurement errors.
†Referred to as the "relative response" (*RR*)

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reaction period, after which each mixture was demonstrated, by iodometric methods, to contain residual chlorine. This residual was quenched by adding sodium arsenite crystals, which were determined in a previous study[7] to have no adverse effect on analysis for total organic halide. Blanks were prepared by subjecting deionized-distilled water to an identical procedure.

Sample workup. The procedure used in this study for extraction and preparation of samples to be analyzed by GC-MS is similar to that described by Christman.[7] Measured 300-mL aliquots of each quenched-reaction mixture, drinking water sample, and blank were spiked with precise amounts of $^{13}C_1$-trichloroacetic acid,* ^{13}C-chloroform,† or both to predetermined concentrations.

Stock solutions of $^{13}C_1$-TCAA and ^{13}C-$CHCl_3$ were made up in deionized-distilled water and methanol, respectively. After these internal standards had been allowed to equilibrate with the sample matrix for at least 2 h, each aqueous solution was acidified to pH 0.7 with concentrated HCl and extracted with three 100-mL aliquots of redistilled diethyl ether. The resulting ether extracts were dried by liquid nitrogen freezing and overnight equilibration with Soxhlet-extracted magnesium sulfate and concentrated to 10 mL in a Kuderna-Danish apparatus. A 5-mL aliquot of this concentrate was methylated with excess diazomethane.[15] Any further concentration of samples was achieved by evaporating the ether with a gentle stream of dry nitrogen. One of the advantages of the method is that special procedures for quantitative recovery of either $CHCl_3$ or TCAA are unnecessary.

Standard solutions for generating calibration curves were prepared by spiking varying amounts of unlabeled $CHCl_3$ and TCAA along with constant amounts of each labeled analogue into 300-mL aliquots of the appropriate sample matrix. The standards utilized were of the highest purity commercially available and were used without further purification. To reduce calibration bias, standard solutions were subjected to the same workup as samples.

GC-MS analysis. The GC-MS system consisted of a double-focusing mass spectrometer of Nier-Johnson geometry‡ interfaced to a dedicated capillary gas chromatograph,§ which was equipped with a capillary on-column injector.** A 98.4-ft (30-m) fused silica capillary column†† was used. Data acquisition and manipulation were totally automated.‡‡ The mass spectrometer was also capable of voltage switching selected ion monitoring (SIM) under the control of a digital scanner. A second system of similar configuration, on which no SIM experiments were performed, was utilized in some of the verification experiments.§§

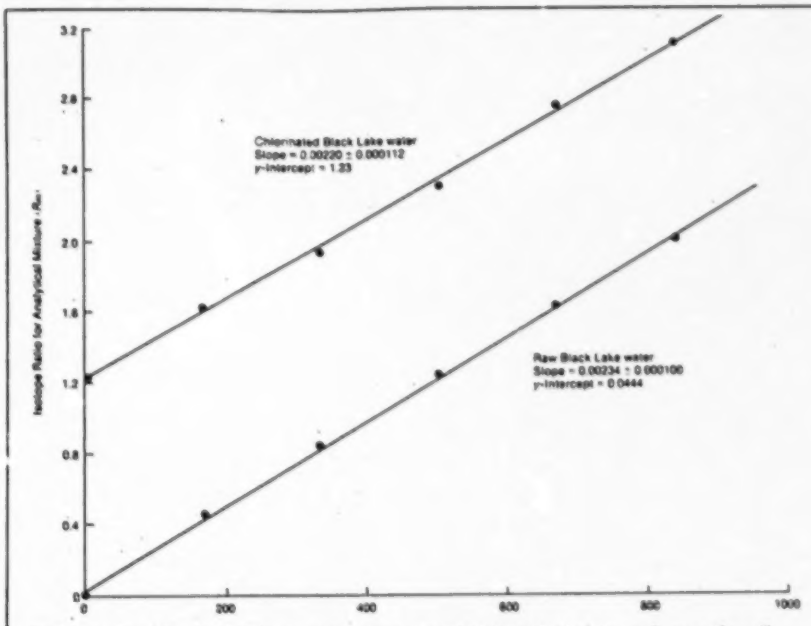

Figure 1. Standard-addition experiment for TCAA (*chlorine-to-carbon ratio—2*)

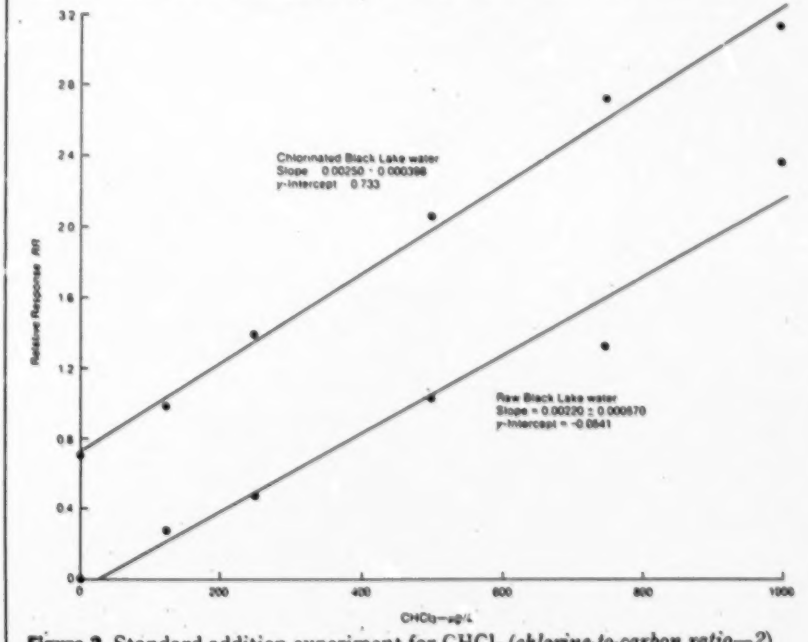

Figure 2. Standard-addition experiment for $CHCl_3$ (*chlorine-to-carbon ratio—2*)

Each concentrated, methylated ether extract was analyzed by capillary column GC-MS utilizing an isotope dilution method to quantitate TCAA and $CHCl_3$. One of two separate data acquisition modes was employed, depending on the particular experiment. The first mode involved collecting complete mass spectra, with ion area ratios being derived from selected mass chromatograms (extracted ion current profiles). The second data acquisition mode involved SIM. In both cases area ratios derived from ions at masses 141 and 142 (methyl trichloroacetate and methyl-^{13}C-trichloroacetate) and 85 and 86 ($CHCl_3$ and $^{13}CHCl_3$) were calculated for standards and samples.

The optimum instrumental conditions for acquisition of complete mass spectra

*KOR Inc., Cambridge, Mass.
†Cambridge Isotopes Inc., Cambridge, Mass.
‡VG7070F, VG Analytical Ltd., Altrincham, Cheshire, UK
§HP5710A, Hewlett-Packard Inc., Avondale, Pa.
**SGE 0C1-2, Scientific Glass and Engineering, Austin, Texas
††DB-1, J&W Scientific Inc., Rancho Cordova, Calif.
‡‡VG2035 data system, VG Analytical Ltd., Altrincham, Cheshire, UK
§§VG7070E, VG2050 data system, VG Analytical Ltd., Altrincham, Cheshire, UK

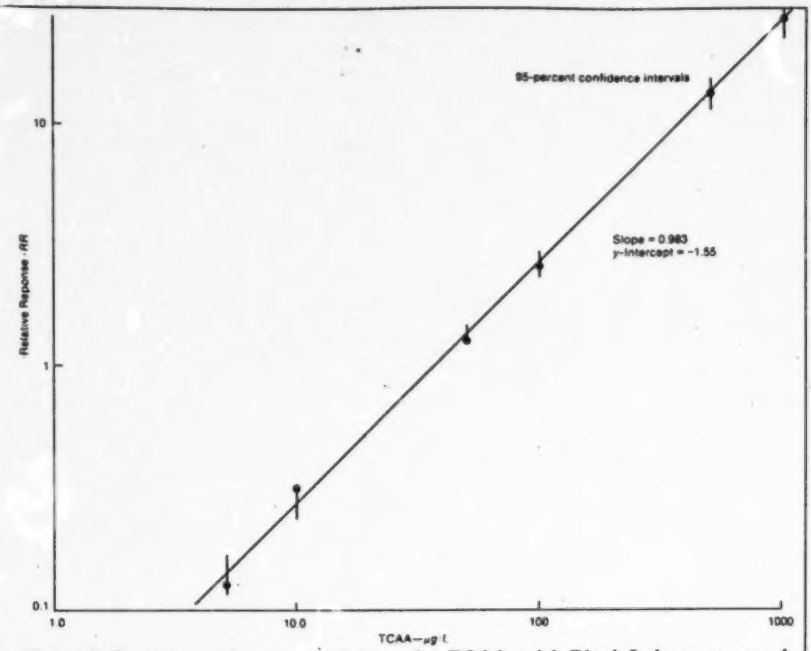

Figure 3. Representative standard curve for TCAA, with Black Lake water used as a surrogate matrix

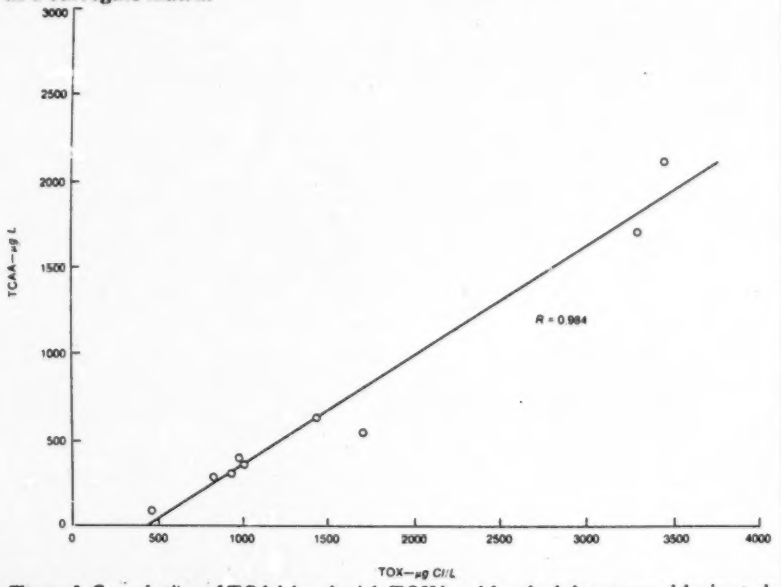

Figure 4. Correlation of TCAA level with TOX level for the laboratory-chlorinated raw water samples

have been described elsewhere.[7] The mass spectrometer was operated in the electron ionization (EI) mode with 70-eV electrons, a 200-μA trap current, and a 4-kV accelerating potential (6 kV in the second system) at a mass resolving power of 1000 (10-percent valley definition). The exponential scan rate was 0.7 s/mass decade over the mass range 350–50, with a reset time of 0.5 s. This was sufficient to obtain approximately eight samples per GC peak and produce a relative standard deviation of 5 percent or less for calculated peak area ratios.

In the SIM mode, the instrumental conditions were the same except that only three ions were monitored in each GC run by rapid switching of the accelerating voltage. Two were from the analyte and either labeled TCAA or $CHCl_3$, and the third was a reference ion produced from methyl benzoate, which was continuously leaked into the ion source from a direct inlet system. Dwell time in the reference ion channel was 50 ms with a channel delay of 50 ms. Parameters for the analyte channels were 100 ms and 50 ms, respectively. Again, relative standard deviations for ion area ratios were generally ≤5 percent.

In all GC-MS runs, 1-2 μL of ether extract were injected on-column at room temperature. After solvent elution, the temperature was raised to 60°C, held 2 min, and then programmed at 6°C/min until methyl trichloroacetate eluted.

Measured ion area ratios were converted to mole ratios and corrected for potential isotope overlap with formulas described by Colby et al[16] (Table 1). Since the methyl esters of TCAA and its labeled analogue coelute on the capillary GC, isotope overlap can produce nonlinearity at the upper and lower ends of standard curves. This is also true of $CHCl_3$ and its labeled analogue. Standard linear regression techniques were used to obtain slopes, intercepts, confidence intervals, and corresponding line equations for standard curves.

Results and discussion

Verification studies. Verification has been defined as "the general process used to decide whether a method in question is capable of producing accurate and reliable data."[17] Several experimental procedures can be utilized for method verification. In this study, the method of standard additions was adopted. The results of two such experiments are shown in Figures 1 and 2. The traces in Figure 1 were derived by spiking known ratios of the labeled and unlabeled acids into Black Lake water over the range 100–1000 μg/L, followed by extraction and methylation as described previously. The internal standard was spiked at a constant 500 μg/L. Data were obtained by collecting complete mass spectra and computing the ratios based on areas derived from selected mass chromatograms of the ions of interest. The measurement range was such that Eq 1 in Table 1 could be utilized.

Linearity of the lower curve establishes that the raw water matrix exerts no bias for either isotope, and its extension to the zero intercept means that no ^{12}C-TCAA was present in the raw water. The increased ratio measured at the zero intercept of the upper curve is due to the ^{12}C-TCAA formed during chlorination, and linearity of this curve shows that the chlorinated water matrix exerts no bias for either isotope. The parallel nature of the two curves in Figure 1 (within the 95-percent confidence interval) shows that no relative bias is exerted by either matrix and justifies confidence in the zero intercept value.

Figure 2 shows a similar standard-addition experiment for $CHCl_3$, the matrixes again being raw and chlorinated Black Lake water. Because of the sharpness of the $CHCl_3$ peak, the SIM technique was utilized for data acquisition. This allowed a greater number of data points to be collected across each GC

TABLE 2
Raw water sources

Source	Type	TOC mg/L	Comments
Lake Waccamaw	Natural	8.64	Coastal plain location; some surrounding development
Lake Singletary	Natural	6.58	Coastal plain location; remote
Black Lake	Natural	3.77	Coastal plain location; surrounding area under development
Lake Wheeler	Impoundment	5.17	Near Raleigh, N.C.
Lake Michie	Impoundment	4.28	Near Durham, N.C.
University Lake	Impoundment	1.41	Near Chapel Hill, N.C.; protected
Haw River	River	3.23	Pittsboro, N.C.; significant industrial and agricultural input
Cape Fear River	River	4.77	Sanford, N.C.; Haw River supplies
Cape Fear River	River	3.61	Fayetteville, N.C.; downstream from Sanford

TABLE 3
Results of chlorinated raw water analyses

Source	TCAA μg/L	$CHCl_3$ μg/L	TOX μg Cl/L	Percent of TOX Accounted for by TCAA and $CHCl_3$
Lake Waccamaw	1720*	670	3280	52.4
Lake Singletary	2120*	849	3440	62.2
Black Lake	319	358	940	56.2
Lake Wheeler	551	301	1700	36.9
Lake Michie	642	342	1430	50.6
University Lake	94.6	89.3	460	30.7
Haw River (Pittsboro, N.C.)	282	222	825	46.3
Cape Fear River (Sanford, N.C.)	389	290	990	51.7
Cape Fear River (Fayetteville, N.C.)	368	295	1000	50.3

*Off standard curve; acceptable application window criteria violated

TABLE 4
Drinking water sources

Locality	Source	Type	Comments
Raleigh, N.C.	Lake Wheeler	Impoundment	Sampled in October 1983; chlorinated raw water previously analyzed
Durham, N.C.	Lake Michie	Impoundment	
Chapel Hill, N.C.	University Lake	Impoundment	
Pittsboro, N.C.	Haw River	River	
Sanford, N.C.	Cape Fear River	River	
Fayetteville, N.C.	Cape Fear River	River	
Washington, D.C.	Potomac River	River	Sampled in April 1984
Richmond, Va.	James River	River	
New Bern, N.C.	Cove City, N.C.	Groundwater	
Emerald Isle, N.C.	Bogue Banks, N.C.	Groundwater	

TABLE 5
Results of drinking water analyses

Locality	TCAA μg/L	TOX μg Cl/L	Percent of TOX Accounted for by TCAA
Raleigh, N.C.	24.5 (21.5-26.5*)	382	4.18
Durham, N.C.	44.0 (39.0-47.0)	378	7.58
Chapel Hill, N.C.	40.3 (35.9-43.7)	403	6.52
Pittsboro, N.C.	52.0 (46.5-56.0)	501	7.76
Sanford, N.C.	20.5 (18.1-22.1)	325	4.11
Fayetteville, N.C.	16.2 (14.4-17.8)	248	4.26
Washington, D.C.	23.4 (18.3-30.0)	146	10.4
Richmond, Va.	36.1 (28.5-46.5)	310	7.59
New Bern, N.C.	4.23 (3.20-5.20)	156	1.77
Emerald Isle, N.C.	53.8 (42.0-67.0)	506	6.19

*Estimated error range based on the 95-percent prediction interval for the appropriate standard curves; the prediction interval represents overall uncertainty, including bias and precision

peak, thus increasing precision in the ion area ratio measurements. The concentration range and spiking level for the internal standard were the same as for the TCAA experiment. The degree of isotope overlap necessitated the use of Eq 2 in Table 1 for plotting data.

In general, the same conclusions can be drawn from Figure 2 as were drawn from Figure 1. It should be noted, however, that the confidence intervals for the slopes in Figure 2 are wider as a result of scatter in the data points, which decreases the level of confidence in the verification. Throughout this study, $CHCl_3$ standard curves showed lower precision compared with the corresponding TCAA curves. The difference in precision is believed to result from differential losses in the spiking procedure, although no experiments were undertaken to demonstrate this.

Analysis of chlorinated raw water samples. In order to demonstrate the applicability of this method, raw water samples were collected, chlorinated in the laboratory, and analyzed for TCAA, $CHCl_3$, and TOX. The sources selected included three major types of North Carolina natural waters (Table 2). The first group represented the "Carolina bay lakes," which are located on the North Carolina coastal plain, are highly colored, and contain high levels of TOC. These include Lake Singletary, Lake Waccamaw, and Black Lake. Fulvic acid isolated from Black Lake water had previously been shown to yield large quantities of hydrophilic chlorinated reaction products and $CHCl_3$.[7] The second group represented impoundments that are used as drinking water supplies and included Lake Wheeler (Raleigh, N.C.); Lake Michie (Durham, N.C.); and University Lake (Chapel Hill, N.C.). The third group represented rivers that are used as drinking water supplies and included the Haw River (Pittsboro, N.C.) and the Cape Fear River, sampled at two locations (Sanford and Fayetteville, N.C.).

Chlorination reactions were carried out at high chlorine-to-carbon mole ratios (4:1) in order to maximize the production of organohalides. A blank was prepared by adding 2.00 mL (~1.53 m*M*) of aqueous hypochlorite to 1 L of distilled-deionized water. This chlorine concentration corresponded approximately to the middle of the range of concentrations used for the raw water samples. Since the range of TCAA and $CHCl_3$ yields was anticipated to be greater than one order of magnitude, standard curves were constructed that covered an increased range of analyte concentration. A representative standard curve for TCAA is shown as a log-log plot in Figure 3. The standard curves for $CHCl_3$ are similar to those for TCAA. Labeled internal standards were spiked at approximately 50 μg/L, and analytes were spiked over the range of 5

to 1000 μg/L. In this particular experiment, distilled-deionized water was used as a surrogate matrix for generating the TCAA standard curve. However, because this water was shown to contain approximately 100 μg $CHCl_3$/L, raw water from Black Lake was used for the $CHCl_3$ standard curve. Analysis of TCAA showed no apparent difference in these two matrixes.

The standard curve in Figure 3 is linear over approximately three orders of magnitude in TCAA concentration (5 to 1000 μg/L), with a slope of 1 (0.983) and a *y*-intercept near the origin (0.0285). The points shown are actual spiked standard values, and the line is derived from the log-weighted linear regression on these points. For standard curves covering this range of concentration, it is necessary to utilize this weighted linear regression to overcome nonlinearity problems, which are discussed in detail by Schoeller.[18] The type of regression utilized in each case (unweighted or log-weighted) depended on the concentration range and visual inspection of the plotted regression line, as well as raw data points.

The results of these analyses are presented in Table 3. Significant quantities of TCAA, $CHCl_3$, and TOX were produced from the majority of sources studied. In this context, "significant" is defined in terms of USEPA's 100-μg/L standard for THMs.[19] Of special interest is the observation that the concentration of TCAA generally exceeded that of $CHCl_3$. These two components accounted for a significant fraction of the measured TOX. Insignificant amounts of organohalides were detected in the blank.

Analysis of drinking water samples. The organohalide results for chlorinated raw water prompted an investigation of actual community drinking waters in order to compare TCAA and TOX levels. Samples were taken from taps in the distribution systems and included three major source types (Table 4). No additional chlorine was added to these samples. Some of the raw water sources for these drinking waters corresponded with those utilized in the previous set of experiments. Analysis of these samples was divided into two parts, with each sample group having its own set of spiked standards (raw Black Lake water surrogate matrix) and standard curve.

The results of these analyses show that TCAA was detected at the low microgram-per-litre level in all drinking water samples (Table 5). It thus appears that TCAA is ubiquitous in finished waters that are disinfected with aqueous chlorine. Uden and Miller[11] reported TCAA values (0 h) of 33.6 and 161 μg/L in two Amherst, Mass., field-quenched tap water samples, which had been analyzed by liquid-liquid extraction and plasma emission GC. The results obtained with isotope dilution GC-MS compare favorably with these values.

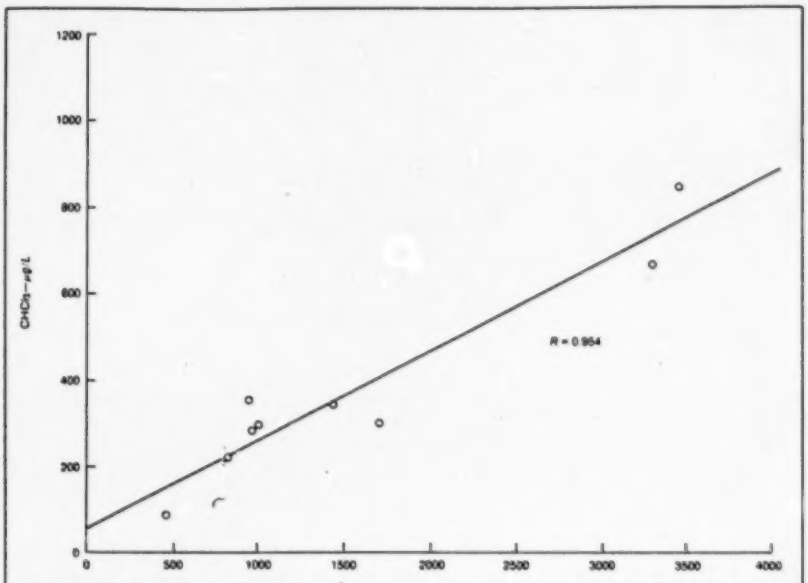

Figure 5. Correlation of $CHCl_3$ level with TOX level for the laboratory-chlorinated raw water samples

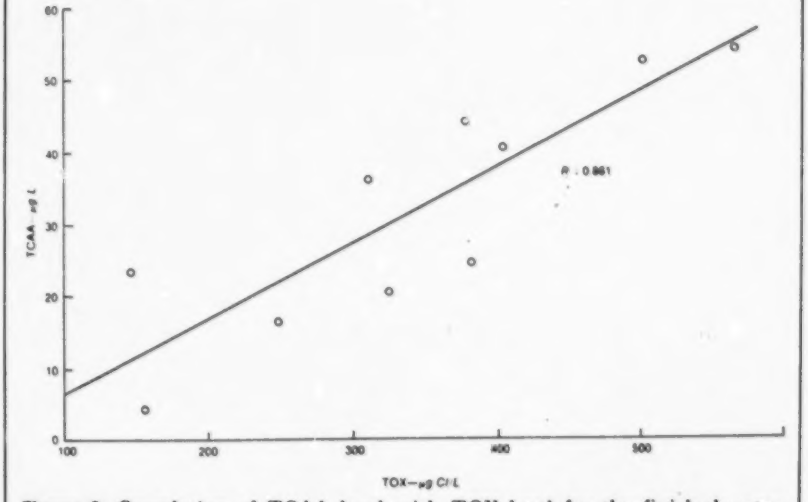

Figure 6. Correlation of TCAA level with TOX level for the finished-water samples

It is instructive to compare the organohalide levels in the finished water with those in the corresponding laboratory-chlorinated raw water. In all cases, TCAA and TOX levels were lower in the actual drinking water samples. Several factors may be responsible for this. First, the chlorine levels in the laboratory reactions were higher (4:1 chlorine-to-carbon mole ratio) than those used in the typical treatment plant. Second, other treatment practices, such as sedimentation, filtration, and addition of other oxidants (e.g., potassium permanganate at the Sanford plant), would tend to reduce organohalide production by removing precursor materials. Finally, other parameters, such as pH, temperature, and chlorine contact time, were different for the drinking water samples and may have contributed to the lower organohalide values.

It is interesting to compare the percentages of TOX accounted for by TCAA in corresponding drinking water and laboratory-chlorinated samples. In each case the amount of TOX accounted for by TCAA is less in the finished water. For example, in the chlorinated raw water from Sanford, 39.3 percent of the TOX is accounted for by TCAA as compared with 4.00 percent in Sanford finished water. The factors contributing to these relative differences are less apparent than those relating to differences in absolute levels. It is, however, attrac-

tive to assume that if TCAA is a reaction end product (as $CHCl_3$ is thought to be), then the lower chlorine-to-carbon ratios used in water treatment practice would produce intermediate substitution products of greater complexity (macromolecular TOX) as a result of the reduced extent of reaction. Other chlorination experiments demonstrated that the amount of TOX accounted for by TCAA and $CHCl_3$ is a function of chlorine-to-carbon ratio.[20]

Correlations between specific compounds and group parameters. The use of group parameters (e.g., TOX and TOC) as general indicators of organic contaminants has been considered by the USEPA.[19] If some relationship exists between the indicator's value and the level of a specific toxic compound in the water, then it should be possible to establish a maximum contaminant level (MCL) for the indicator and thus regulate the specific compound. This would avoid problems associated with monitoring each compound to enforce individual MCLs. The principle is the same as that of the coliform indicator, which is used for bacterial contamination.

Correlations for the levels of TCAA and $CHCl_3$ with the level of TOX in the laboratory-chlorinated raw water samples appear in Figures 4 and 5, respectively. The correlation coefficients are high ($R = 0.98$ and 0.95, respectively). The correlation for the level of TCAA with the level of TOX in the finished-water samples appears in Figure 6. Even though these samples were taken from different treatment plants that utilized different source waters and different treatment schemes, the correlation is still reasonable ($R = 0.86$). These results suggest that TOX may be a useful indicator parameter for TCAA and perhaps for $CHCl_3$.

Summary and conclusions

This article describes the verification and application of an isotope dilution GC-MS method for determining aqueous TCAA at the microgram-per-litre level. The simultaneous determination of aqueous $CHCl_3$ utilizing the same sample workup procedure was also demonstrated. These two analytes have different chemical and physical properties, and neither is recovered quantitatively by the extraction and concentration procedures adopted. Use of stable isotopically labeled internal standards eliminates the need for quantitative recovery and allows the use of compromise workup procedures. Measurement of recovery, a potential source of bias, is also unnecessary.

Given appropriate internal standards, many other halogenated compounds (dichloroacetic acid and chloral, for example) can be determined without significiant modification to the sample workup procedure. The establishment of MCLs for a large number of chlorination by-products with different chemical and physical properties would make isotope dilution GC-MS an attractive monitoring technique. In choosing an analytical technique for a routine monitoring program, the analyst must decide whether the advantages of precision, accuracy, bias, and simplicity offered by isotope dilution GC-MS are appropriate to the particular situation.

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